

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) IMPROVEMENTS IN FUEL CELL

(71) We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, residing at 1 River Road, Schenectady 12305, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to fuel cells and to a process of generating electricity; more especially to fuel cells with supported and unsupported catalytic anodes in which chemical energy may be converted directly to electrical energy using ammonia fuel, and their use.

As it is well known, fuel cells are devices capable of generating electricity by electrochemically combining an oxidizable reactant, termed a fuel, and a reducible reactant, termed an oxidant. The reactants are fluids, either liquids or gases, and are usually fed continuously to the cell from separate external sources. The fuel cell itself comprises spaced electrodes ionically connected by an electrolyte. It is a characteristic of fuel cells that the electrodes and electrolyte remain substantially chemically invariant in use. Each electrode is electronically conductive, adsorbs the fuel or oxidant employed, presents catalyst materials for the electrode reaction, and does not oxidize unduly under the operating conditions of the cell.

When fuel and oxidant are concurrently and separately supplied to the different electrodes of a fuel cell, an electrical potential will develop across the electrodes. When an electrical load is provided across the electrode, an electrical current flows therebetween, the electrical energy thus represented being generated by the electro-catalytic oxidation of fuel at one electrode and the simultaneous electro-catalytic reduction of oxidant at the other.

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Electrode support materials are materials which are electronically conductive, support catalyst material for electrode reaction, and adsorb the fuel or oxidant employed, and do not oxidize unduly under operating conditions of a fuel cell. Of various electrode support materials, we prefer to utilize graphite, boron carbide, tantalum boride, titanium boride, and metallic silicides.

Since the adsorption of gases on solids is a surface phenomena, it is desirable that the electrodes be of the maximum practicable surface area and that the surface of the catalyst material preferably be in its most active state for the adsorption of gases. Thus, the extent and character of the surface presented by such catalytic material in a fuel cell electrode is an important factor in the securing of superior electrode performance. It is, of course, possible to ensure an extensive catalytically active surface in a fuel cell electrode by utilizing large quantities of catalytically active material. However, the most highly catalytically active materials are expensive, and accordingly, these catalytic materials should be utilized in as efficient manner as possible.

The most efficient utilization of catalyst is achieved by distributing the catalytic materials so that the greatest amount of surface area may be secured per unit weight of the catalytic material. This is the reason for previous deposition of catalytic material on a metallic base or support. The support material, in addition to having a high resistance to electrochemical oxidation and having a high resistance to attack by strong acids, must be electrically conducting.

The present invention provides a fuel cell comprising an air electrode, an air oxidant, an electrolyte, an ammonia fuel, and a fuel electrode comprising a catalyst of a platinum-iridium alloy containing at least 20 weight percent of iridium.

The fuel cell of the present invention may be constructed in such a way that the catalyst

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is dispersed on an electrode support material (e.g. boron carbide, graphite, tantalum or titanium borides and metallic silicides), the catalyst loading being from 2 to 10 milligrams of catalyst per square centimeter of active area; alternatively, the construction of the fuel electrode may be such that the electrode support material is dispensed with (i.e. the catalyst is said to be unsupported), the catalyst loading being from 10 to 34 milligrams of catalyst per square centimeter of active area.

When a fuel electrode is employed in which the catalyst is dispersed on an electrode support material, it is preferred to provide a terminal grid covered with the support material.

The fuel electrode in the fuel cell of the present invention is preferably constructed in such a way that a hydrophobic film is bonded to one surface of the electrode.

The present invention also provides a process of generating electricity which comprises providing an air electrode, providing a fuel electrode spaced from the air electrode, the fuel electrode comprising a catalyst of a platinum-iridium alloy containing at least 20 weight percent of iridium, providing an electrolyte communicating with the electrodes, supplying an air oxidant to the air electrode, supplying an ammonia fuel to the fuel electrode and connecting an electrical load across the electrodes to produce electrical energy.

The features and advantages of the invention will be better understood from the following description taken in connection with the accompanying drawing in which:

FIGURE 1 is a sectional view of a fuel cell made in accordance with our invention;

FIGURE 2 is an enlarged fragmentary sectional view of a fuel cell electrode made in accordance with our invention;

FIGURE 3 is a plot comparing the performance, in fuel cells with an ammonia fuel, of two electrodes constituted by a boron carbide electrode support material with respective catalysts dispersed thereon of (i) 20 weight percent of an alloy of platinum and iridium (in the proportion of 1:1 by weight) and (ii) 20 weight percent platinum with respective loadings of 6.6 and 6.7 milligrams of metal per square centimeter;

FIGURE 4 is a plot comparing the performance, in fuel cells with an ammonia fuel, of two electrodes constituted by a boron carbide electrode support material with respective catalysts dispersed thereon of (i) 20 weight percent platinum and (ii) 20 weight percent of an alloy of platinum and iridium (in the proportion of 4:1 by weight) with respective loadings of 6.7 and 6.8 milligrams of metal per square centimeter.

FIGURE 5 is a plot comparing the performance in fuel cells with an ammonia fuel, of three electrodes constituted by a graphite electrode support material with respective

catalysts dispersed thereon of (i) 20 weight percent platinum, (ii) 20 weight percent of an alloy of platinum and iridium (in the proportion of 4:1 by weight), and (iii) 27 weight percent of an alloy of platinum and iridium (in the proportion of 1:1 by weight) with respective loadings of 6.2, 6.6 and 5.5 milligrams of metal per square centimeter.

FIGURE 6 is a plot comparing the performance, in fuel cells with an ammonia fuel, of two electrodes with catalysts of platinum and platinum-51 weight percent iridium alloy and with metal loadings of 34 and 51 milligrams of metal per square centimeter, respectively.

FIGURE 7 is a plot comparing the performance, in fuel cells with an ammonia fuel, of two electrodes with catalysts of platinum and platinum-21.3 weight percent iridium alloy with metal loadings of 51 and 34 milligrams of metal per square centimeter, respectively.

It is to be noted that in Figures 3 to 7 the abbreviation "NM" means noble metal.

In FIGURE 1 of the drawing there is shown generally at 10 a fuel cell embodying our invention which comprises an anode 11 and a cathode 12, separated by an annular electrolyte gasket 13. An electrolyte inlet conduit 14 and an electrolyte outlet conduit 15 are sealingly related to the electrolyte gasket to circulate a free aqueous electrolyte to and from an electrolyte chamber 16 formed by the anode, cathode and gasket. An anode gasket 17 and a cathode gasket 18 are positioned adjacent opposite faces of the electrolyte gasket to seal therewith and to hold the anode and cathode in assembled relation. Identical end plates 19 and 20 are associated with the anode and cathode gaskets, respectively, in sealing relation therewith. To hold the gaskets and end plates in assembled relation a plurality of tie bolts 21 are provided, each having a threaded end 22 and a nut 23 mounted thereon. To insure against any possibility of internal short circuiting of the fuel cell electrodes, the tie bolts are provided with insulative bushings 24 within each end plate and with an insulative washer 25 adjacent each terminus.

An oxidant chamber 26 is formed by the cathode gasket, cathode, and end plate 20. An oxidant inlet conduit 27 is sealingly associated with the end plate to allow oxidant to be fed to the oxidant chamber while an oxidant outlet conduit 28, which is optional, is similarly associated with the end plate to allow the purge of oxidant. It is recognized that where the fuel cell is to be operated on ambient air it is unnecessary that the fuel cell include any conduits for delivering oxidant to the cathode. The anode, anode gasket, and end plate 19 similarly cooperate to form a fuel chamber 29. A fuel outlet conduit 30, similar to oxidant outlet conduit 28, is provided. A fuel inlet conduit 31 is shown for

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providing an ammonia fuel to the fuel chamber from a fuel source 32, schematically shown.

In FIGURE 2 of the drawing there is shown generally a fuel cell anode 11 embodying our invention which as a grid in the form of a metal wire screen 33 which serves the functions of transmitting electrical current and providing reinforcement for the electrode. An electrical connection in the form of an electrical lead 34 is connected directly to screen 33. Lead 34 passes to the outside of fuel cell 10 as shown in FIGURE 1 at the interface of gasket 17 and gasket 13, which elements form part of the fuel cell housing. Electrode 11 has an electrode support material 35 with a gas adsorbing iridium or platinum-iridium alloy catalyst dispersed thereon held together by a binder material such as, for example, an aqueous suspension of polytetrafluoroethylene or polychlorotrifluoroethylene. This material 35 surrounds both the screen 33 and a portion of electrical lead 34. Other organic and inorganic binders may be employed in electrode 11 with the choice of such binder depending upon operating conditions such as temperature, electrolyte, and pressure. The ratio of such a binder to the mixture of catalyst and support material may be from 5 to 50% by weight, with the preferred range being from 10 to 30% by weight. A hydrophobic film 36 is bonded to one surface of material 35 to prevent electrolyte flow through electrode 10.

The electrode support material is selected from a wide variety of materials including graphite, boron carbide, metallic silicides, and certain metallic borides. We have found that suitable metallic silicides include titanium silicide, tungsten silicide, zirconium silicide, vanadium silicide, tantalum silicide, chromium silicide, and molybdenum silicide, while suitable metallic borides include tantalum boride and titanium boride. While metallic silicides are generally suitable, certain metallic borides (e.g. chromium boride, nickel boride, molybdenum boride) corrode in the electrolyte and are thus not considered desirable.

The above platinum-iridium alloy catalyst of our fuel cell electrode is particularly useful in fuel cells employing an ammonia fuel and an alkaline electrolyte.

While the current collecting grid is incorporated into the electrode as is shown in FIGURE 2, the grid can also be pressed against the surface of the electrode. Such grids, which require material of good electrical conductivity, can be provided in various configurations such as screens, metal wires, metal bars, punched metal plate, expanded metal plate and porous metal sheet.

The fuel cell anode used in our invention can also be formed of a catalyst which has not been dispersed on an electrode support material, i.e. a so-called unsupported catalyst. In this construction as in the construction of

FIGURE 2, a grid in the form of a metal wire screen 33 is provided for transmitting an electrical current and producing reinforcement for the electrode. An electrical connection in the form of an electrical lead 34 is connected directly to the screen. Lead 34 passes to the outside of fuel cell 10 as shown in FIGURE 1 at the interface of gasket 17 and gasket 13, which elements form part of the fuel cell housing. The electrode has a catalyst of iridium or of platinum-iridium held together by a binder material such as, for example, an aqueous suspension of polytetrafluoroethylene (PTFE). The catalyst was formed by blending the catalyst material into a PTFE-water suspension. This suspension was spread on a 1 7/8 inch diameter platinum screen which was 45×45 mesh and had a wire diameter of 0.0078 inch so that the paste extended into and through the screen mesh openings. A platinum tab for electrical connection in the fuel cell extended from the screen. After the electrode was dried slowly, one surface thereof was waterproofed by spraying with a hydrophobic film employing a Teflon (Registered Trade Mark) suspension. The loadings were in the range of from 10 to 34 milligrams per square centimeter of active area.

The preferred electrolyte for use in a fuel cell employing our improved electrode is an alkaline electrolyte such as potassium hydroxide. Other alkaline electrolytes may be employed which are suitable for fuel cell operation below 300°C. Such electrolytes include solutions of other alkali-metal hydroxides, and alkali-metal carbonates.

The finding that the above platinum-iridium alloy catalyst electrode operates effectively with an ammonia fuel in a fuel cell was quite unexpected since catalysts are highly specific in their behaviour toward fuels of different types. Low catalyst loading could also be employed providing excellent operation in a fuel cell and a substantial reduction in the cost of the electrode.

In an illustrative formation and operation of electrode anodes as shown in FIGURES 1 and 2 and the formation and operation of a fuel cell as shown in FIGURE 1 of the drawing, solutions were prepared containing platinum "P" salt of the formula $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ and iridium chloride of the formula IrCl_3 , the amounts being such as to ensure the presence of at least 20 weight percent of iridium in the resulting alloy. Boron carbide powder or graphite was intimately mixed with the mixed salt solution and the paste was evaporated to dryness under a heat lamp. Each dry catalyst was then ground and sieved through a 400 mesh nylon screen having 45 holes/lineal inch. Finally, the catalyst was reduced in flowing hydrogen at 125°C in a tube furnace for three hours and then cooled in a stream of nitrogen. The resulting gas adsorbing catalysts were of platinum-iridium

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alloy dispersed on boron carbide and graphite support materials.

- 5 In addition to the above preparation platinum-iridium alloy (containing at least 20 weight percent of iridium) catalysts were also prepared starting from solutions of chloro-platinic acid of the formula H_2PtCl_6 and of a halide of iridium.

- 10 The above dried electrode material was mixed with a polytetrafluoroethylene (PTFE) suspension containing 59% solids. A paste, formed in this manner, was mixed thoroughly and then spread on a 1 7/8 inch diameter platinum screen which was 45×45 mesh and had a wire diameter of 0.0078 inch so that the paste extended into and through the screen mesh openings. A platinum tab for electrical connection in the fuel cell extended from the screen. Several electrodes were formed and dried slowly on a hot plate in air and then in a desiccator overnight. Each of the electrodes was then waterproofed on one side by spraying with a hydrophobic film on one surface employing a suspension of 2.25 milliliters of a 1:7 polytetrafluoroethylene water suspension on a 5×5 inch area. The alloy loadings were in the range from 2 to 10 milligrams per square centimeter of active area.

- 30 One of the above electrodes, which was constituted by an alloy of platinum-iridium, containing 20 weight percent of iridium, dispersed on a boron carbide electrode support material (20 weight percent alloy 80 weight percent boron carbide) with a metal loading of 6.8 milligrams of metal per square centimeter of active area, was then employed as an anode in a fuel cell while a standard platinum black electrode, which has 34 milligrams of platinum per square centimeter bonded with PTFE was employed as a cathode. The cell was operated with oxygen gas to the cathode and an ammonia fuel. The hydrophobic film surface of the anode faced the ammonia gas stream. A 54% (w/w) potassium hydroxide was used as the electrolyte and the cell was operated at a temperature of 100°C. This cell operated quite satisfactorily and its operation will be discussed below in connection with FIGURE 4 of the drawing.

- 50 In FIGURE of the drawing, there is a graph comparing the performance, in fuel cells with an ammonia fuel, of two electrodes constituted by a boron carbide electrode support material with respective catalysts dispersed thereon of (i) 20 weight percent of an alloy of platinum and iridium (in the proportion of 1:1 by weight) and (ii) 20 weight percent platinum with respective metal loadings of 6.6 and 6.7 milligrams of metal per square centimeter of active area. The current density in milliamperes per square centimeter is plotted against cell voltage (iR-free) in volts. The improved performance is shown for the fuel cell with the 20 weight percent of the said

65 alloy of platinum and iridium on the boron carbide support material.

In FIGURE 4 of the drawing, there is a graph comparing the performance, in fuel cells with an ammonia fuel, of two electrodes constituted by a boron carbide electrode support material with respective catalysts dispersed thereon of (i) 20 weight percent platinum and (ii) 20 weight percent of an alloy of platinum and iridium (in the proportion of 4:1 by weight) with respective metal loadings of 6.7 and 6.8 milligrams of metal per square centimeter of active area. The current density of milliamperes per square centimeter is plotted against an anode reference in volts. The good performance is shown for the fuel cell with 20 weight percent of the said alloy of platinum and iridium.

In FIGURE 5 of the drawing, there is a graph comparing the performance, in fuel cells with an ammonia fuel, of three electrodes constituted by a graphite electrode support material with respective catalysts dispersed thereon of (i) 20 weight percent platinum, (ii) 20 weight percent of an alloy of platinum and iridium (in the proportion of 4:1 by weight), and (iii) 27 weight percent of an alloy of platinum and iridium (in the proportion of 1:1 by weight) with respective metal loadings of 6.2, 6.6 and 5.5 milligrams of metal per square centimeter of active area. The current density in milliamperes per square centimeter is plotted against an anode reference in volts. The good performance is shown for the fuel cell with the said alloy catalysts dispersed on graphite electrode support material.

In FIGURE 6 of the drawing there is a graph comparing the performance, in fuel cells with an ammonia fuel, of electrodes with unsupported catalysts of platinum and platinum-51 weight percent iridium alloy with respective metal loadings of 34 and 51 milligrams of metal per square centimeter of active area. The current density in milliamperes per square centimeter is plotted against cell voltage (iR-free) in volts. The improved performance is shown for the fuel cell with the unsupported alloy catalyst.

In FIGURE 7 of the drawing there is a graph comparing the performance, in fuel cells with an ammonia fuel, of electrodes with unsupported catalysts of platinum and platinum-21.3 weight percent iridium alloy with respective metal loadings of 51 and 34 milligrams of metal per square centimeter of active area. A current density in milliamperes per square centimeter is plotted against an anode reference in volts. The good performance is shown for the fuel cell with the alloy catalyst.

WHAT WE CLAIM IS:—

1. A fuel cell comprising an air electrode, an air oxidant, an electrolyte, an ammonia fuel, and a fuel electrode comprising a catalyst of

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a platinum-iridium alloy containing at least 20 weight percent of iridium.

5 2. A fuel cell according to Claim 1, in which the catalyst is dispersed on an electrode support material, and the catalyst loading is from 2 to 10 milligrams of catalyst per square centimeter of active area.

10 3. A fuel cell according to Claim 1, in which the catalyst is unsupported by any electrode support material, and the catalyst loading is from 10 to 34 milligrams of catalyst per square centimeter of active area.

15 4. A fuel cell according to Claim 1 or 2, in which there is provided a terminal grid covered with electrode support material on which the catalyst is dispersed.

20 5. A fuel cell according to any one of Claims 1 to 4, in which hydrophobic film is bonded to one surface of the electrode.

25 6. A fuel cell according to Claim 5, in which the air electrode is a bonded platinum electrode with a platinum loading of 34 milligrams of platinum per square centimeter of active area, and the electrolyte is potassium hydroxide.

7. A fuel cell according to Claim 1 constructed and arranged substantially as herein described and shown in Figures 1 and 2 of the accompanying drawings.

8. A process of generating electricity which 30 comprises providing an air electrode, providing a fuel electrode spaced from the air electrode, the fuel electrode comprising a catalyst of a platinum-iridium alloy containing at least 20 weight percent of iridium, providing an 35 electrolyte communicating with the electrodes, supplying an air oxidant to the air electrode, supplying an ammonia fuel to the fuel electrode and connecting an electrical load across the electrodes to produce electrical energy. 40

9. A process according to Claim 8 substantially as herein described by reference to the specific description relating to any one of Figures 3 to 7 of the accompanying drawings.

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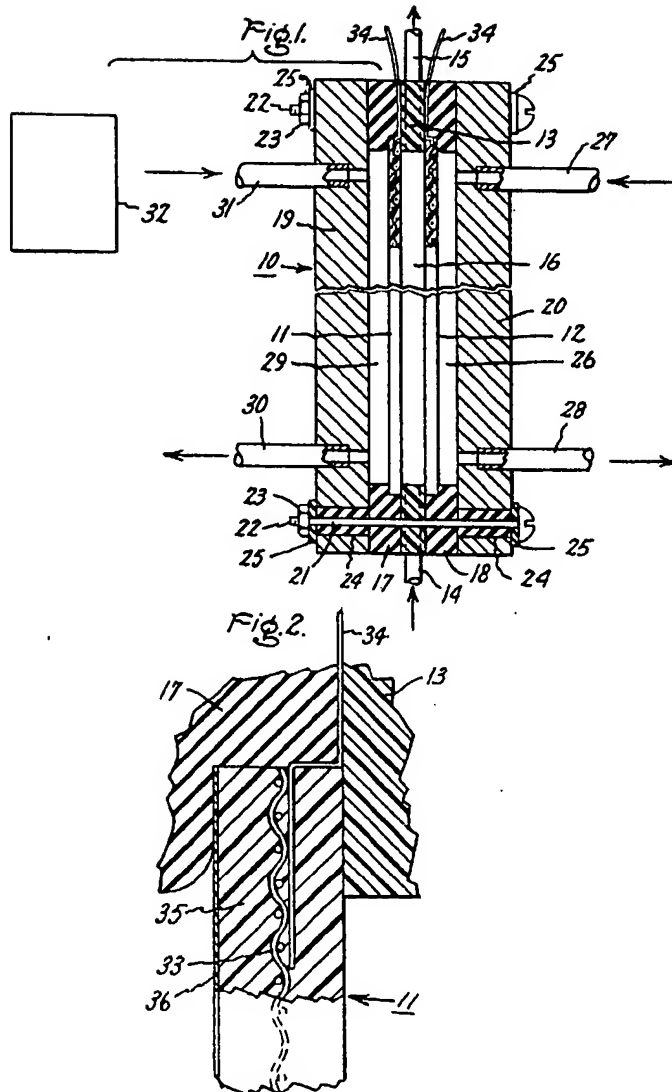
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Sheet 1



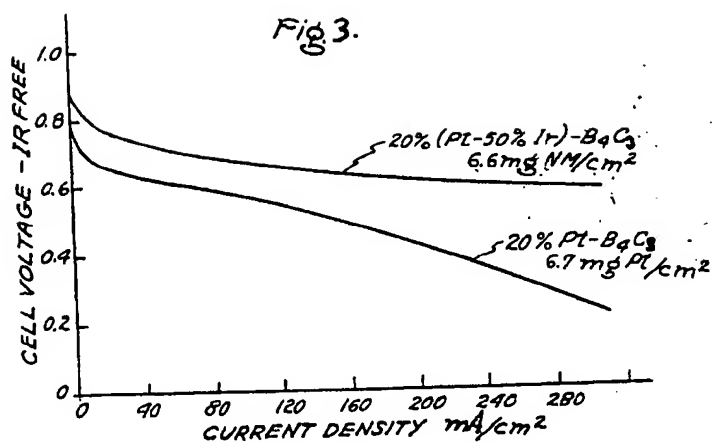
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Fig. 6.

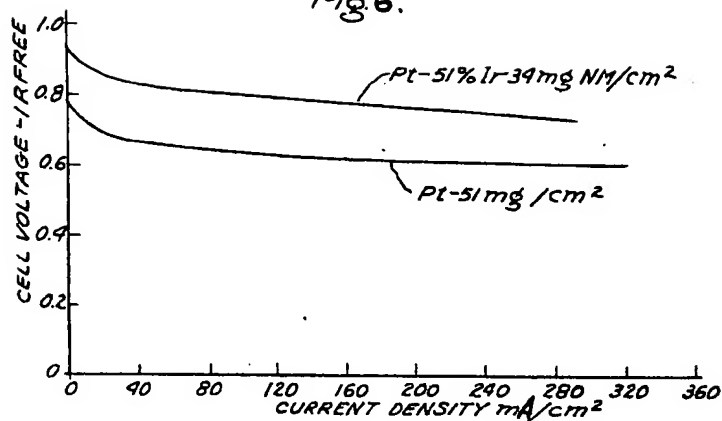
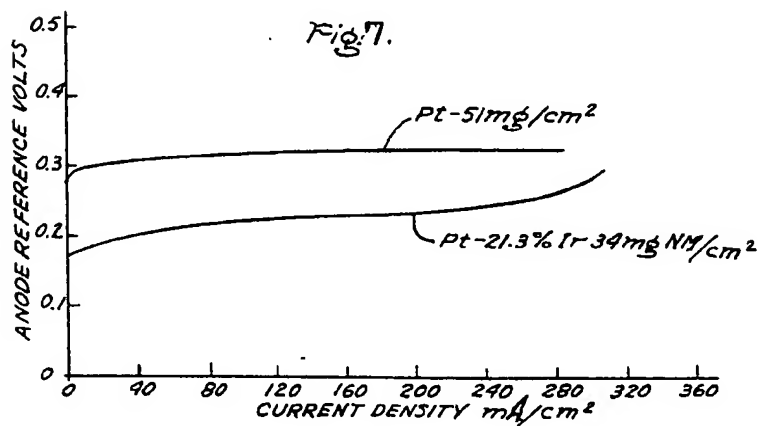


Fig. 7.



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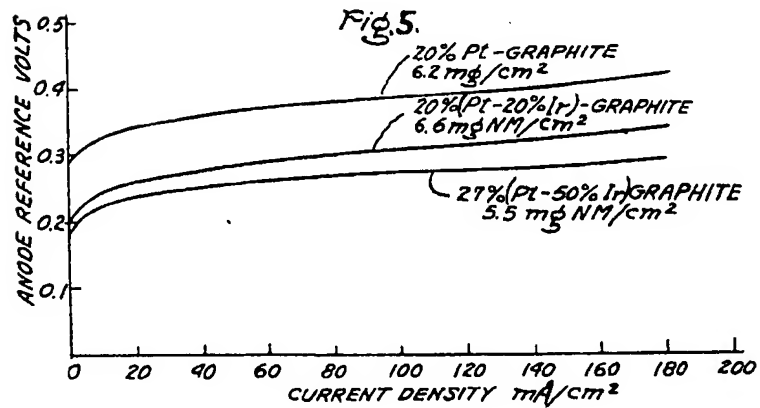
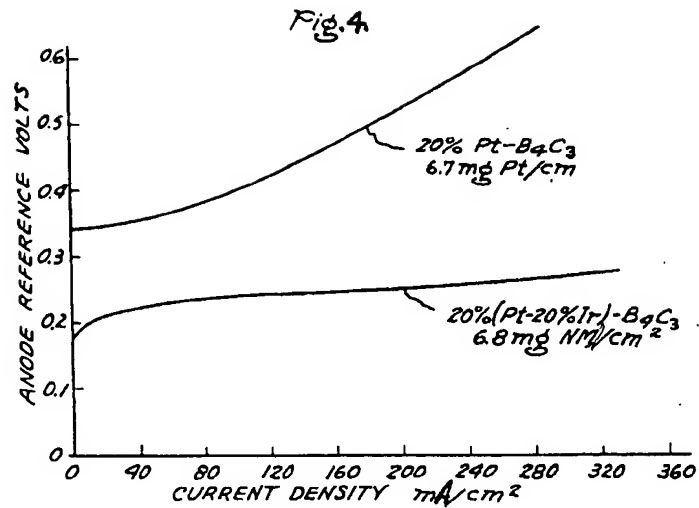
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